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Problem of "Vertical" Correlation in Pi-Electron Systems*

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The problem of "vertical" correlation is re-examined. Defined in terms of the two-electron probability distribution function, "vertical" correlation is separated from the related "in–out" correlation effect. A study is made of the planar methyl anion and its isoelectronic analog, the planar ammonia molecule, to assess the importance of sigma antibonding orbitals for the correlation of the $2p_z^2$ pair. These contribute -0.092 eV for planar CH_3^- and -0.120 eV for planar NH_3. The implications for Σ–Π separability are discussed.

INTRODUCTION

IN recent years much study has been devoted to the problem of pi-electron correlation.[1] As a first approximation a conjugated molecule can be described by an antisymmetrized product of doubly filled pi LCAO MO's with at most one or two electrons outside closed shells. The presence of a sigma core is expressed either explicitly as a further set of occupied orbitals or implicitly in the energy calculation. When expanded in terms of the constituent atomic orbitals, this type of wavefunction yields a sum of covalent terms and ionic terms (terms which represent two pi electrons being located in the same region of space). These ionic terms represent states of relatively high interelectronic repulsion. As in the historic example of the hydrogen molecule,[2] a better energy can be obtained by reducing their relative importance. For the typical pi-electron system this is achieved either by a selective configuration interaction with excited states built out of the various antibonding pi orbitals (AMO method[3]) or by using a more general starting wavefunction wherein electrons of different spins occupy slightly different spatial MO's (NPSO treatment[4]). These methods introduce a certain "horizontal" correlation between the positions of the various pi electrons along the conjugated chain,[5] leading to a reduction in the interelectronic repulsion energy. However, this increased constraint on the electronic motion slightly augments the total system kinetic energy, as predicted by the virial theorem.[6]

Although reduced in magnitude, the partial ionic character remains. One would expect that the situation could be improved by introducing an appropriate correlation directly into the ionic terms. It is this residual correlation which was once thought to be responsible for the large discrepancy between the theoretical value of the one-center electrostatic repulsion integral, 16.93 eV,[7] and the often adopted semiempirical value of 10.6 eV.[8] This semiempirical value is obtained from the energetics of the carbon disproportion reaction

$$C\cdot + C\cdot \rightarrow C: + C^+. \qquad (1)$$

Hermann[9] has carried out a careful study of Reaction (1) using a Hartree–Fock open-shell calculation for the unhybridized valence states of neutral carbon $(1s^2 2s 2p^2 2p_z)$; carbon negative ion $(1s^2 2s 2p^2 2p_z^2)$; and carbon positive ion $(1s^2 2s 2p^2)$. More recently Orloff and Sinanoğlu[10] performed a similar calculation using hybridized valence states with a sigma core of the form $1s^2 tr^3$. Here tr^3 represents three electrons with one electron in each of three equivalent trigonal hybrid orbitals. These particular valence states are chosen to simulate the conditions existing in an actual pi-electron system. The discrepancy between the various γ_{pp} is found to arise mainly from the large change in both the pi $(2p_z)$ and sigma (tr) orbitals in going from C· to C:. The corrected "theoretical" value becomes ~12.5 eV. Various considerations lead Orloff and Sinanoğlu to estimate the correlation energy of the $2p_z^2$ pair to be only ~ -1 eV.[11] It is just this problem of the correlation energy of the $2p_z^2$ pair in the carbon negative ion, either isolated or in a molecular environment, that we chose to discuss here.

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[1] For an excellent review see R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963). See also L. Salem, *Molecular Orbital Theory of Conjugated Systems* (W. A. Benjamin, Inc., New York, 1966), p. 81.

[2] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

[3] R. Pauncz, *Molecular Orbitals in Chemistry, Physics, and Biology. A Tribute to R. S. Mulliken* (Academic Press Inc., New York, 1964), p. 433.

[4] D. M. Hirst and J. W. Linnett, J. Chem. Phys. **43**, 574 (1965).

[5] For a study of the correlation effects introduced by the AMO method, see W. H. Adams, J. Chem. Phys. **39**, 23 (1963).

[6] P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959).

[7] Calculated with a Slater $2p$ orbital with $\zeta = 1.59$.

[8] G. Pilcher and H. A. Skinner, J. Inorg. Nucl. Chem. **24**, 937 (1962).

[9] R. B. Hermann, J. Chem. Phys. **42**, 1027 (1965).

[10] M. K. Orloff and O. Sinanoğlu, J. Chem. Phys. **43**, 49 (1965).

[11] In agreement with the estimation of this quantity by V. McKoy and O. Sinanoğlu, J. Chem. Phys. **41**, 2689 (1964),

GENERAL TREATMENT OF THE PROBLEM

A starting wavefunction may be written in the form

$$^1\Psi_0 = \mathcal{A}_{\Sigma\Pi}[\psi_{\text{core}} 2p_z(1)\, 2p_z(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)], \tag{2}$$

where ψ_{core} is an unspecified antisymmetric core wavefunction and $\mathcal{A}_{\Sigma\Pi}$ is an antisymmetrization operator between the sigma and pi sets, namely,

$$\mathcal{A}_{\Sigma\Pi} = [1/(N!)^{1/2}] \sum_{\Sigma\Pi} (-1)^{p_{\Sigma\Pi}} P_{\Sigma\Pi},$$

N being the total number of permutations between the sigma and pi sets. Neglecting the core we may consider the simultaneous probability of finding one pi electron at a particular point (r_1, θ_1, ϕ_1) while the other is at (r_2, θ_2, ϕ_2). This two-electron probability distribution function, the spinless second order pi electron density matrix,[12] is for Wavefunction (2)

$$\rho_2^{\pi}(r_1, \theta_1, \phi_1; r_2, \theta_2, \phi_2) = 2p_z(1)\, 2p_z(2). \tag{3}$$

The effect of an introduced correlation term is easiest seen in the consequent change in this two-electron distribution.

A sufficiently general way to treat the correlation of the $2p_z^2$ pair is to write as a correlated wavefunction[13]

$$\begin{aligned} ^1\Psi = \mathcal{A}_{\Sigma\Pi}\psi_{\text{core}}\{ & C_1 2p_z(1)\, 2p_z(2) + C_2\psi_s(1)\psi_s(2) \\ & + C_3\psi_p(1)\psi_p(2) + C_4\psi_d(1)\psi_d(2) + \cdots \\ & + C_n[\psi_s'(1)\psi_d'(2) - \psi_d'(1)\psi_s'(2)]\} \\ & \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \end{aligned} \tag{4}$$

Here ψ_s, ψ_s', ψ_p, ψ_d, $\psi_d' \cdots$ are unspecified orbitals having s, p, $d \cdots$ character with respect to the carbon atom as origin. These orbitals are dependent on certain parameters which, together with the coefficients C_i are varied to minimize the total energy.

The correlation introduced by (4) and the corresponding change in the two-electron distribution, are mainly of two kinds. First is a radial, or "in–out," effect in which the change in the two-electron distribution reflects a tendency for the two pi electrons to be simultaneously at different radial distances from the carbon nucleus without any angular correlation between their positions. That is

$$\Delta\rho_2^{\pi}(r_1, \theta_1, \phi_1; r_2, \theta_2, \phi_2) = \Delta\rho_2^{\pi}(r_1, \theta_1, \phi_1; r_2, \theta_2 + \pi, \phi_2). \tag{5}$$

It is easily verified that this radical correlation arises from the terms in (4) containing orbitals which have the same *antisymmetry* with respect to reflection as the original $2p_z$ orbital. Hermann,[9] using an optimized doubly excited $3p_z^2$ configuration, finds a lowering of -0.42 eV arising from just such a radial effect.

We notice that this radial correlation could be easily combined with either of the methods outlined above for horizontal correlation. In the AMO treatment this could be achieved by using antibonding orbitals with orbital exponents differing slightly from those of the bonding orbitals.[14] A similar result could be obtained in the NPSO framework by using molecular spin orbitals which differ not only in the MO coefficients but also in the orbital exponents of the constituent atomic orbitals.

The second important kind of correlation effect introduced by a wavefunction such as (4) is an azimuthal or "vertical" effect. Here the change in the two-electron density matrix reflects primarily an increased tendency for the two pi electrons to be simultaneously on opposite sides of the molecular plane. In other words

$$\Delta\rho_2^{\pi}(r_1, \theta_1, \phi_1; r_2, \theta_2, \phi_2) \neq \Delta\rho_2^{\pi}(r_1, \theta_1, \phi_1; r_2, \theta_2 + \pi, \phi_2). \tag{6}$$

It is seen that this "vertical" correlation arises from the terms in (4) containing orbitals which are *symmetric* with respect to reflection in the nodal plane of the $2p_z$ orbital.

VERTICAL CORRELATION IN THE ISOLATED CARBON NEGATIVE ION

Originally Dewar and various collaborators[15] proposed locating the two pi electrons of the $2p_z^2$ configuration in the individual lobes of the $2p_z$ orbital in order to introduce the pi–pi correlation then believed lacking. This "*split-p*" technique would correspond to the "vertical" (azimuthal) correlation described above. Initial results augured well for the idea—placing the two pi electrons separately into "upper" and "lower" p lobes gave a value for the one-center repulsion integral close to the semi-empirical value.[16] (However, as we have seen above, the discrepancy in the values of γ_{pp} is largely due to reasons other than direct pi–pi correlation. Thus Dewar's original method overcorrelated the pi electrons.) It was not long before several authors pointed out[17] that Dewar's idea suffered from the grave defect that the "upper" and "lower" p lobes when taken separately are not orthogonal to the sigma core. Saturno, Joy, and Snyder[18] orthogonalized the split orbital to a representative core ($1s^2 2s^2$) and found that a resulting large increase in kinetic energy

[12] R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

[13] Because of computational complexity we exclude a treatment involving direct introduction of the interelectronic distance.

[14] This idea is closely related to a study of the excitation energies of ethylene by S. Huzinaga, J. Chem. Phys. **36**, 453 (1962).

[15] See, for example, M. J. S. Dewar and H. N. Schmeising, Tetrahedron **5**, 166 (1959); **11**, 96 (1960).

[16] M. J. S. Dewar and C. E. Wulfman, J. Chem. Phys. **29**, 158 (1958).

[17] J. S. Griffith, J. Chem. Phys. **36**, 1689 (1962); C. A. Coulson and C. S. Sharma, Proc. Roy. Soc. (London) **A272**, 1 (1963).

[18] A. F. Saturno, H. W. Joy, and L. C. Snyder, J. Chem. Phys. **38**, 2494 (1962).

greatly outweighed the energy lowering due to vertical correlation.

Why this occurs becomes obvious when we look at an expansion of the "upper" p-lobe[19]:

$$\psi_{\text{upper}}=(1/\sqrt{2})2p_z+(\tfrac{3}{8})^{1/2}2s'+(\tfrac{15}{128})^{1/2}2d_{z^2}'+\cdots, \quad (7)$$

where all the orbitals have the same orbital exponent. Since the "upper" and "lower" lobes have a sizeable $2s$ component, the presence of a sigma core (itself with $2s$ character) leads to an immediate violation of the Pauli principle. Renormalization, as in the above-mentioned calculation, alleviates this but only at the loss of the energetically important $2s'$ component. This result is quite general for any calculation of this type performed on an isolated carbon atom or negative ion–any $2s$ component in a wavefunction of Type (4) is forbidden by the exclusion principle. One can, of course, use (4) without its $2s$ components. This has been done under several forms; the reported "vertical" correlation contributions are collected in Table I. We remark the relative importance of d-type contributions, specifically $3d^2_{z^2}$. The $3s^2$ and $3s3d_{z^2}$ contributions are small, probably a consequence of the two radial nodes in the $3s$ orbital.

What we need, then, to augment the "vertical" correlation energy lowering is a low-lying s-type orbital which nonetheless is orthogonal to the core. We are thus led to consider the importance of the sigma antibonding orbitals. These orbitals, orthogonal to the core sigma orbitals because of a node along the bond length, behave in the molecular plane like $3s$ or $4s$ atomic orbitals. Yet in the direction perpendicular to the molecular plane (in the region of the $2p_z^2$ pair) the sigma antibonding orbitals have the desired $2s$ character. For an isolated carbon atom the sigma bonding and antibonding orbitals become indistinguishable.

TABLE I. "Vertical" correlation contribution of various excited configurations.

Excited configuration contributing to (4)	Energy lowering (eV)
Dewar (nonorthogonal)	−5.95[a]
Dewar (orthogonalized)	−0.073[a]
$3d_{z^2}$	−0.108,[b] −0.150,[c] −0.148[d]
$3s^2$	−0.025,[b] −0.038[d]
$3s3d_{z^2}$	−0.000[b]
Total for C^-	−0.133[b]
$(CH^*)^2$	−0.092[e]

[a] Reference 18 of text, $\zeta_{2s}=1.4793$, $\zeta_{2p}=1.59$.
[b] Reference 9 of text, $\zeta_{3d}=1.67$.
[c] J. P. Lowe, J. Chem. Phys. **41**, 502 (1964). GMS calculation using $\zeta_{2p}=1.50$, $\zeta_{3d}=2.10$.
[d] H. Joy, Rev. Mod. Phys. **35**, 602 (1963).
[e] This paper, calculation performed for the CH_3^- molecule.

[19] J. A. R. Coope, Rev. Mod. Phys. **35**, 600 (1963).

We thus want to study the carbon atom in a molecular environment which distinguishes between the sigma bonding and antibonding orbitals in order to assess the importance of the latter for "vertical" correlation.

VERTICAL CORRELATION IN THE PLANAR METHYL ANION

At this point let us consider the (hypothetical) planar methyl anion (CH_3^-). In this simple case, we should be able to evaluate the importance of the sigma antibonding orbitals for "vertical" correlation. The hydrogens are assumed coplanar at 120° to one another. An approximate ground-state wavefunction may be written as

$$^1\Psi_0=\mathcal{A}_{2\Pi}\{\psi_{\text{core}}2p_z(1)2p_z(2)\}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}, \quad (2)$$

where, here,

$$\psi_{\text{core}}=|\,1s_c1\bar{s}_c\sigma_1\bar{\sigma}_1\sigma_2\bar{\sigma}_2\sigma_3\bar{\sigma}_3\,|. \quad (8)$$

The σ's are three equivalent sigma bonding orbitals. These we approximate as a simple combination of a trigonal sp^2 hybrid orbital on the carbon atom and a single $1s$ orbital ($\zeta=1$) on the hydrogen, namely,

$$\sigma_i=N_\sigma\{a\,tr_i+b\,h_i\}, \quad (9)$$

N_σ being a normalization constant. The parameters a and b determine the bond polarity.

We consider, in analogy to (4), double excitations of the form $2p_z^2\rightarrow\sigma^{*2}$, where σ^* is a corresponding sigma antibonding orbital

$$\sigma_i^*=N_\sigma^*\{a'tr_i-b'h_i\}. \quad (10)$$

For the CH_3^- system this would correspond to a double $\pi\rightarrow CH^*$ excitation. The correct excited state to use has the form

$$^1\Psi_1=(1/\sqrt{3})\mathcal{A}_{2\Pi}\{\psi_{\text{core}}[\sigma_1^*(1)\sigma_1^*(2)+\sigma_2^*(1)\sigma_2^*(2)+\sigma_3^*(1)\sigma_3^*(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]\}. \quad (11)$$

It is easy to see that (11) represents a virtual double excitation capable of introducing correlation of the "vertical" type between the pi electrons. For this excitation the nondiagonal matrix element has the simple form

$$H_{01}=\frac{1}{\sqrt{3}}\sum_{i=1}^{3}[2p_z\sigma_i^*\mid 2p_z\sigma_i^*].$$

To first order the corresponding energy lowering is

$$\Delta W=-H_{01}^2/(E_{\Psi_1}-E_{\Psi_0}). \quad (12)$$

For the case of the isolated C^- ion in its valence state where σ_i and σ_i^* collapse to the same atomic orbital, a virtual excitation of the type considered here, bringing in $2s$ character, is, as we have seen, forbidden by the Pauli principle. In the actual CH_3^- molecule, however, the orbitals σ_i and σ_i^* are distinct, orthogonal molecular

orbitals. Although the antibonding orbital has a certain amount of $3s$ and $4s$ character in the molecular plane, perpendicular to this plane σ_i^* has the single node characteristic of the $2s$ atomic orbital. There should be a further "vertical" contribution to the correlation energy of the $2p_z^2$ pair arising from mixing with the sigma antibonding orbitals which will not appear in the case of an isolated carbon negative ion.

We take a C–H bond length of 1.102 Å.[20] Using the Pople and Santry treatment[21] for this distance, we obtain for the CH bonding orbital

$$\sigma_i = N_\sigma\{1.058\, tr_i + 0.942\, h_i\}. \quad (13)$$

By the requirement of orbital orthogonality we obtain for σ_i^*

$$\sigma_i^* = N_\sigma\{0.990\, tr_i - 1.010\, h_i\}. \quad (14)$$

Using the values of certain required integrals as tabulated by Pitzer,[20] we find after some straightforward algebra that $H_{01} = 0.0467$ a.u.

The Pople and Santry theory is based on parameters taken from the neutral carbon atom in its valence state. Perhaps CH_3^- should be examined instead in terms of parameters taken from the appropriate carbon negative ion valence state (V_3).[22] Under consideration of the probable modifications, we do not expect H_{01} to change greatly.

There remains the important question of what excitation energy to use in (12). Recently Robin, Hart, and Keubler[23] identified the low-lying olefin "mystery" band at 6–7 eV as a one-electron $\pi \rightarrow CH^*$ transition. It is just a two-electron excitation of this sort which leads to our chosen wavefunction (11). In the Appendix we show how it is possible to relate the excitation energy for such a two-electron excitation to the single excitation energy. We obtain

$$\Delta W_{\text{double}} = 2\Delta W_{\text{single}} + J_{p,p} + J_{\sigma^*,\sigma^*} - 2J_{p,\sigma^*} - 2K_{p,\sigma^*}, \quad (15)$$

where $J_{A,B}$ and $K_{A,B}$ are the usual two-electron repulsion and exchange integrals, namely,

$$J_{A,B} = \int A^\dagger(1) B^\dagger(2) \frac{1}{r_{12}} A(1) B(2)\, dv_1 dv_2,$$

$$K_{A,B} = \int A^\dagger(1) B^\dagger(2) \frac{1}{r_{12}} B(1) A(2)\, dv_1 dv_2.$$

Using the experimental value of the single excitation energy of 6.5 eV and calculated values of the required electrostatic integrals,[24] we obtain a double excitation energy of 0.6451 a.u. These values yield an energy lowering of −0.092 eV due to a "vertical" correlation of the $2p_z^2$ pair arising from a double virtual excitation to the unoccupied sigma antibonding orbitals. It is interesting to note that the contribution of these antibonding orbitals is of almost equal importance with the $3d_z^2$[22] contribution in the case of the isolated C^- ion (Table I).

VERTICAL CORRELATION IN THE PLANAR AMMONIA MOLECULE

This system, isoelectronic with the planar CH_3^- molecule, has been treated in detail by Kaplan.[25] Since the correlation of the $2p_z^2$ pair is of the "dynamical" type,[11,26] we would expect the corresponding correlation energy to rest approximately unchanged from the value of ∼−1 eV for the carbon $2p_z^2$ pair. A ground-state wavefunction for the ammonia molecule in its planar configuration may be written as

$$^1\Psi_0 = |\, 1a_{1g} 1\bar{a}_{1g} 2a_{1g} 2\bar{a}_{1g} 1e_x 1\bar{e}_x 1e_y 1\bar{e}_y 2p_z 2\bar{p}_z \,|, \quad (16)$$

where the filled orbitals are the lowest energy symmetry adapted molecular orbitals belonging to the covering group D_{3h}. A "vertical" correlation effect, analagous to that studied in the previous section, may be introduced by the double excitation $2a_{1g}^2 \rightarrow 3a_{1g}^2$. This last orbital is an antibonding sigma orbital having the form

$$3a_{1g} = -0.1491\, 1s_n + 1.3723\, 2s_n - 1.5230\, H_0, \quad (17)$$

where H_0 is the normalized totally symmetric combination of the three hydrogen $1s$ orbitals.

Using Kaplan's values for the pertinent integrals and orbital energies, we find an energy lowering of −0.120 eV due to "vertical" correlation arising from a pi→ sigma antibonding double virtual excitation. This is in good agreement with the result of the previous section. We should notice that the same effect could be expected for an analagous isoelectronic molecule, the hydronium ion H_3O^+ in its planar configuration.

DISCUSSION

We have seen that in the case of the planar methyl anion and its isoelectronic analog, the planar ammonia molecule, interaction between the doubly filled $2p_z$ orbital and certain sigma antibonding orbitals leads to a "vertical" correlation energy lowering of ∼−0.1 eV. It would be tempting to add this to the known energy lowerings arising from $3d_z^2$- and $3s^2$-type excitations in the case of the C^- ion (Table I). This,

[20] This distance, that of a C (sp^3)–H bond, is only slightly longer than the corresponding sp^2 distance of 1.06 Å (see Ref. 21 of this paper). The sp^3 distance was chosen to permit using the numerical results of R. M. Pitzer, thesis, Harvard University, 1963, for our required numerical calculations.

[21] J. A. Pople and D. P. Santry, Mol. Phys. **9**, 301 (1965).

[22] H. A. Skinner and H. O. Pritchard, Trans. Faraday Soc. **49**, 1254 (1953).

[23] M. R. Robin, R. R. Hart, and N. A. Keubler, J. Chem. Phys. **44**, 1803 (1966).

[24] We find $J_{p,p} = 0.6360$ a.u., $J_{\sigma^*,\sigma^*} = 0.5536$ a.u., $J_{p,\sigma^*} = 0.4842$ a.u., and $K_{p,\sigma^*} = 0.02694$ a.u.

[25] H. Kaplan, J. Chem. Phys. **26**, 1704 (1957). Recently there has been some doubt of the accuracy of Kaplan's total energy, see B. D. Joshi, J. Chem. Phys. **43**, 840 (1965). We believe this would not change our conclusions here.

[26] O. Sinanoğlu, Advan. Chem. Phys. **6**, 315 (1964).

however, cannot be done, for the σ^* orbital is orthogonal to neither the $3s$ nor the $3d_z$ atomic orbitals. The overlap between σ^* and a $3d_z$ atomic orbital with exponent 1.67[9] is -0.39; the overlap between σ^* and a representative $3s$ orbital is somewhat larger, about 0.5.[27] It may be that the σ^* orbital plays the same role for the CH_3^- molecule that the $3s$ orbital plays in the case of the C^- ion.[28] The σ^* and $3d_z^2$ contributions appear to be reasonably distinct. In conclusion we might estimate that "vertical" correlation contributes between -0.2 and -0.3 eV to the correlation energy of the $2p_z^2$ pair.

In an actual conjugated system two pi electrons of opposite spin have a large probability of being in the same region of space only in the ionic component of the total wavefunction. For a neutral system these ionic terms have about equal weight with the covalent terms in which neither radial nor "vertical" correlation is likely to be important.[29] As a crude estimate we may thus say that, over all, "vertical" correlation contributes a lowering of ~ -0.12 eV per pi-electron pair in a conjugated system.

We see that Dewar, in attributing the whole of pi-electron correlation to a "vertical" effect,[30] overestimates its importance. Nevertheless, "vertical" correlation does contribute to pi-electron correlation in conjugated systems to an extent somewhat greater than the original pessimistic estimate of Saturno, Joy, and Snyder.[18]

What is important is that "vertical" correlation arises partially from a virtual double excitation to sigma antibonding orbitals. This has important implications for the problem of Σ–Π separability. This approximation, basic to most treatments of conjugated systems and first elaborated by Lykos and Parr a decade ago,[31] states that the wavefunction for a pi-electron system may be written as

$$\Psi = \mathfrak{A}_{\Sigma\Pi}(\psi_\Sigma \psi_\Pi), \tag{18}$$

where $\psi_\Sigma(\psi_\Pi)$ is some unspecified antisymmetric function of the sigma (pi) electrons. *The sigma and pi wavefunctions are independent in the sense that no one-electron orbital may contribute to both of these sets.* Already put into doubt by the work of Orloff and Sinanoğlu,[10] this set of approximations is further questioned, although to a lesser degree, by our results. In a more refined study of the core wavefunction, a configuration interaction including selected $\sigma \rightarrow \sigma^*$ virtual excitations is certain to be important. Yet *it is just these sigma antibonding orbitals which we find to contribute to the pi-electron correlation energy.* The separability conditions thus seem violated. We note, however, that the same holds true for the $3p_z^2$, $3s^2$, and $3d_{z^2}^2$ contributions to the $2p_z^2$ correlation which *seem* not to violate the Σ–Π conditions. However, these orbitals will certainly intervene in an accurate treatment of the core.

[27] Here it is the *magnitude*, not the *sign*, of the overlap integral which is important.

[28] This interesting suggestion was made by the referee.

[29] This can be shown by considering the small variation in the interelectronic distance, $(1/r_{12})$ between two electrons constrained in two $2p_z$ orbitals on different carbon atoms—whatever the relative "vertical" coordinates of the two electrons.

[30] A. L. H. Chung, M. J. S. Dewar, and N. L. Sabelli, Ref. 3, p. 395.

[31] P. G. Lykos and R. Parr, J. Chem. Phys. **24**, 1166 (1956).

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The author would like to thank Dr. Lionel Salem for having suggested this problem and having been the source of much helpful criticism. He would also like to thank Dr. Roland Lefebvre for critical discussion and the National Science Foundation for financial support in the form of a predoctoral fellowship.

The author would like to express his gratitude to the referee for several pertinent comments and suggestions.

APPENDIX

We consider a system of $2N$ electrons described by a closed-shell determinantal wavefunction of the form

$$^1\Psi_0 = |\, \phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_j\bar{\phi}_j\cdots\phi_N\bar{\phi}_N\,|, \tag{A1}$$

where the ϕ_i's are an ensemble of unspecified orthonormal spatial orbitals. We consider single and double excitations of the type $\phi_j \rightarrow \phi_k$ and $\phi_j^2 \rightarrow \phi_k^2$, ϕ_j and ϕ_k being, respectively, occupied and unoccupied in the original determinant (A1). In analogy with Hartree–Fock theory[32] we define ϵ_j as the energy of an occupied orbital

$$\epsilon_j = I_j + \sum_{i \neq j}^{N} (2J_{i,j} - K_{i,j}) - J_{j,j}. \tag{A2}$$

I_j is the one-electron energy of ϕ_j, and $J_{A,B}$ and $K_{A,B}$ are the usual electrostatic repulsion and exchange integrals.

Likewise, for an unoccupied orbital ϕ_k, we define

$$\epsilon_k = I_k + \sum_{i=1}^{N} (2J_{i,k} - K_{i,k}), \tag{A3}$$

the sum in this case being over *all* the originally occupied orbitals.

A single excitation $\phi_j \rightarrow \phi_k$ (singlet–singlet) yields the following excited state:

$$^1\Psi_1 = (1/\sqrt{2})\{|\, \phi_1\bar{\phi}_1\cdots\phi_j\bar{\phi}_k\cdots\phi_N\bar{\phi}_N\,| + |\, \phi_1\bar{\phi}_1\cdots\phi_k\bar{\phi}_j\cdots\phi_N\bar{\phi}_N\,|\}. \tag{A4}$$

For this case we find

$$\Delta W_{\text{single}} = (\epsilon_k - \epsilon_j) - J_{j,k} + 2K_{j,k}, \tag{A5}$$

a well-known formula.[33]

A double excitation $\phi_j^2 \rightarrow \phi_k^2$ yields the following

[32] C. C. J. Roothaan, J. Chem. Phys. **23**, 66 (1951).

[33] C. C. J. Roothaan, J. Chem. Phys. **23**, 80 (1951), Eq. (68).

doubly excited state:

$$^1\Psi_2 = |\,\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_k\bar{\phi}_k\cdots\phi_N\bar{\phi}_N\,|. \qquad \text{(A6)}$$

Remembering the definitions of an occupied and unoccupied orbital energy [(A2), (A3)], we find after a little manipulation

$$\Delta W_{\text{double}} = 2(\epsilon_k - \epsilon_j) + J_{k,k} + J_{j,j} - 4J_{j,k} + 2K_{j,k}. \qquad \text{(A7)}$$

Introducing (A5) into (A7), we obtain

$$\Delta W_{\text{double}} = 2\Delta W_{\text{single}} + J_{k,k} + J_{j,j} - 2J_{j,k} - 2K_{j,k}. \qquad \text{(A8)}$$

The excitation energy for a double excitation is seen to be twice the excitation energy for the corresponding single excitation plus a sum of certain electrostatic integrals. From inspection this sum cannot be large; it can be either positive or negative, depending on the particular choice of ϕ_j and ϕ_k.

It goes without saying that this result depends on the assumption that the orbitals not involved in the various excitations do not undergo modifications in the various excited states. A more refined calculation would have to take these second-order changes into account. Most probably, however, these modifications would be small in comparison with those occasioned by the addition or removal of an electron from the system.[10]

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Correlation between Exchanging Electrons

M. H. Alexander and L. Salem

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Correlation between Exchanging Electrons*

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Attempts to introduce overlap and exchange into a purely general study of interatomic or intermolecular long-range forces lead to complicated, physically opaque expressions for the interaction energy. A study is made of a most simple system, two hydrogen atoms at large distances, taking overlap and exchange rigorously into account. This system is especially interesting due to the failure of the Heitler–London wavefunction to describe adequately the lowest-triplet ($^3\Sigma_u^+$)–lowest-singlet ($^1\Sigma_g^+$) separation at very large distances. A formal study separates the interaction energy into a "generalized dispersion" and "generalized exchange–correlation" energy. A many-configuration calculation performed at an internuclear distance of 8 a.u. shows that, whereas certain configurations yield the well-known dispersion energy, other configurations, particularly those of the excited charge-transfer type, correct for the erroneous triplet–singlet separation. This distinction reflects the introduction of two distinct types of correlation effects which are investigated in terms of the two-electron distribution function.

I. INTRODUCTION

MUCH study has been made of the long-range interaction energy between two atoms or molecules under the assumption that electron exchange and overlap between the two systems can be neglected.[1–3] It is only in the last two years that attempts have been made, in a more or less rigorous fashion, to allow for the presence of these two small effects.[4–6] In each of these studies the total wavefunction for the combined but well separated systems is expressed in terms of *antisymmetrized* products of isolated system wavefunctions. The resulting expressions for the total intersystem interaction energy are of such complexity that a separation into physically distinguishable contributions is exceedingly difficult, if not impossible.[4,6] Only in exceptional cases, where the systems remain rigorously orthogonal even when exchange is permitted, does the energy expression break down into separable effects.[5]

In spite of the complexity of the problem, the contribution of exchange and overlap to interatomic or intermolecular energies at large distances can be investigated for certain extremely simple systems. A good case in point is the long-range interaction of two hydrogen atoms. At large distances a seemingly excellent description of the hydrogen molecule is offered by the Heitler–London wavefunction. However, it has been shown, particularly by Herring,[7,8] that the Heitler–London wavefunction, although correct at infinite separation, gives a rather erroneous description at large, but not infinite, distances. The Heitler–London wavefunction predicts a lowest-triplet ($^3\Sigma_u^+$)–lowest-singlet ($^1\Sigma_g^+$) separation which is too small. This separation measures the hypothetical rate of electron exchange between two hydrogen atoms if the electrons were distinguishable. The exact behavior of the lowest singlet and triplet states of the hydrogen molecule at large internuclear distances is shown in Fig. 1.

We attempt in this paper to obtain the true triplet–singlet separation, as well as the absolute energies of both states, by a configuration-interaction treatment using various configurations constructed from antisymmetrized products of orbitals centered on the hydrogen atoms. In the first section we briefly review the initial Heitler–London description as well as Herring's contribution to the problem. The following section is devoted to a general study of how various virtually excited states contribute either to a general lowering of both the singlet and triplet states or to a modification of their initial energy separation. The interaction energy is separated into a "generalized dispersion" energy as well as a "generalized exchange correlation" energy. The fourth section contains the result of an extended many-configuration calculation performed at an interatomic separation of 8 a.u. Whereas certain excited configurations account for the well-known dispersion energy, other states are responsible for an improvement of the Heitler–London triplet–singlet splitting. After a brief discussion of the results of this configuration-interaction treatment, the distinction between the contribution of various excited

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[8] C. Herring, "Direct Exchange between Well-Separated Atoms," in *Magnetism*, G. Rado and H. Suhl, Eds. (Academic Press Inc., New York, to be published).

configurations is restated in terms of electron correlation effects in the concluding section.

II. HEITLER-LONDON APPROXIMATION

At large distances the hydrogen molecule can be simply described by placing the two electrons into the $1s$ orbitals of each of the two hydrogen atoms. Antisymmetrization leads to both a singlet and triplet state of the form

$$^{1(3)}\Psi_0=[1/2(1\pm S_{00}^2)]^{1/2}\{|\,1s_a1\bar{s}_b\,|\pm|\,1s_b1\bar{s}_a\,|\}. \quad (1)$$

Here the plus sign is to be taken for the singlet; the minus sign for the triplet. S_{00} is the one-electron overlap integral between two hydrogen $1s$ orbitals separated by a distance R, the interatomic separation. In the Born–Oppenheimer approximation the appropriate Hamiltonian is

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+r_{12}^{-1}-r_{a1}^{-1}-r_{b1}^{-1}-r_{a2}^{-1}-r_{b2}^{-1}+R^{-1}. \quad (2)$$

The coordinate system used is shown in Fig. 2. We obtain the following well-known result for the singlet and triplet energies,

$$^{1(3)}E_0=[1/(1\pm S_{00}^2)]\{\mathcal{J}_{00}\pm\mathcal{K}_{00}\}. \quad (3)$$

Here $\mathcal{J}_{AB}$ and $\mathcal{K}_{AB}$ are the so-called "Coulomb" and "exchange" integrals, both containing one- and two-electron contributions

$$\mathcal{J}_{AB}=\int A^*(1)B^*(2)HA(1)B(2)\,d\tau_1 d\tau_2,$$

$$\mathcal{K}_{AB}=\int A^*(1)B^*(2)HB(1)A(2)\,d\tau_1 d\tau_2. \quad (4)$$

At large distances we may take the orbital exponent of the $1s$ orbitals equal to unity.[9]

In the Heitler–London approximation the triplet and singlet states are separated by an energy difference given by

$$^3E_0-{}^1E_0=2\{\mathcal{K}_{00}-S_{00}^2\mathcal{J}_{00}\}+\mathcal{O}(S^4), \quad (5)$$

where the presence of an overlap charge density in an energy integral is counted as $\mathcal{O}(S)$. Sugiura[10] has calculated the leading term of Expression (5), finding

$$^3E_0-{}^1E_0=2\{\tfrac{2}{45}-\tfrac{2}{15}(\gamma+\ln R)\}R^3e^{-2R}+\mathcal{O}(R^2e^{-2R}), \quad (6)$$

where γ is Euler's constant.

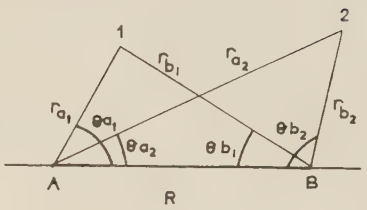

FIG. 2. Coordinate system used (see Ref. 32 of this paper).

The correct asymptotic triplet–singlet splitting has been obtained by Herring and Flicker[8,11] (see also Ref. 12) from a rather intricate perturbation treatment. For details we refer the reader to the original work, giving just the final result here, namely,

$$^3E-{}^1E=1.636R^{5/2}e^{-2R}+\mathcal{O}(R^2e^{-2R}). \quad (7)$$

Good agreement is obtained between this expression and the difference between the very accurate singlet and triplet energies obtained recently by Kołos and Wolniewicz.[13]

The Heitler–London and true triplet–singlet separations are given in Table I for a number of internuclear separations. Also presented are the results of an early calculation by Hirschfelder and Linnett.[14] Examination of Table I reveals that *the Heitler–London splitting is consistently smaller than the true value. The discrepancy becomes worse with increasing interatomic separation.* A quick glance at Eq. (6) shows that the Heitler–London wavefunction actually puts the triplet below the singlet at $R\sim 50$ a.u. This is a physical impossible result, since the lowest energy state for a three-dimensional, N-electron system described by a nonrelativistic, spinless Hamiltonian containing a symmetric potential is the state of lowest total spin.[15] Herring attributes this poor behavior to an *inadequate correlation of the electrons in the exchange region*[8] with the result that the energy of the singlet state is slightly too high. In the triplet state, of course, the electrons are prevented from getting too close to each other by the exclusion principle. The Hirschfelder–Linnett energy separations obtained from essentially a Heitler–London-plus-configuration-interaction treatment are seen to be *smaller* than the Heitler–London results alone, in contrast with the expected improvement. A possible reason for this discrepancy is examined in Sec. IV of this paper.

One might remember that for interactions at medium range, in particular at the equilibrium internuclear distance for the H_2 molecule, the Heitler–London singlet

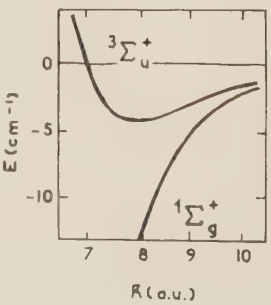

FIG. 1. Potential-energy curves for the lowest singlet and triplet states of H_2 at large internuclear distances, taken from Kołos and Wolniewicz (Ref. 13 of this paper).

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TABLE I. Triplet–singlet separation in H_2 (in a.u.$\times 10^{-6}$).

R (a.u.)	A Heitler-London[a]	B Herring and Flicker[b]	Kołos and Wolniewicz[c]	Hirschfelder and Linnett[d]	Error $(B-A)/B$
7.0	172	176	186	169	2.7%
8.0	31.2	33.3	33.2	30.7	6.4%
9.0	5.48	6.05	5.80	...	9.5%
10.0	0.934	1.066	2.4	0.92	12.4%
11.5	0.0629	0.0753	...	...	16.4%

[a] This paper, Eq. (5). [b] Reference 11 of this paper. [c] Reference 13 of this paper. [d] Reference 14 of this paper.

wavefunction *overcorrelates* the electronic motion.[16] It seems that exactly the opposite is true at large distances. The Heitler–London description becomes erroneous due to the lack of adequate correlation between the two electrons.

III. GENERAL TREATMENT OF THE PROBLEM

In this section we consider the improvement of the Heitler–London wavefunction brought about by the introduction of various virtually excited configurations. As we have seen, the starting singlet and triplet states are represented as

$$^{1(3)}\Psi_0=[2(1\pm S_{00}^2)]^{-1/2}\{|\,1s_a1\bar{s}_b\,|\pm|\,1s_b1\bar{s}_a\,|\}. \quad (1)$$

We take as our manifold of possible excited configurations an ensemble of antisymmetrized products of isolated atom orbitals. These we represent by $\{\phi_i\}$ and $\{\chi_j\}$, which denote a set of orthonormal functions completely spanning the one-electron space of the isolated hydrogen atom and centered, respectively, on the two hydrogen atoms. Instead of using the manifold of discrete plus continuum solutions of the Schrödinger equation for the hydrogen atom, we chose the alternative orthogonal set first proposed by Löwdin and Shull.[17] These orbitals have the form

$$\phi_{r\,lm}=\bar{R}_{nl}(r)\,Y_{lm}(\theta,\phi), \quad (8)$$

where

$$\bar{R}_{nl}(r)=[2^{3/2}/(n+l+1)\,!][(n-l-1)\,!/(n+l+1)\,!]^{1/2}\times(2r)^l L_{n+l+1}{}^{2l+2}(2r)e^{-r},$$

$L_{n+l+1}{}^{2l+2}$ being an associated Laguerre polynomial.[18] The advantages of such a set are twofold. This is a complete discrete set; we thus avoid the necessity of using wave packets built out of the continuum of positive energy solutions for the hydrogen atom. Secondly the maxima of orbitals of Type (8), all having the *same* orbital exponent, do not expand with increasing principal quantum number as do the usual hydrogenic orbitals. This has important implications which we discuss later.

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[17] P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).
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Since the Löwdin–Shull orbitals are not solutions to the Schrödinger equation for the hydrogen atom,[19] we are constrained to use a variational rather than perturbation theoretic treatment. At the large distances under consideration where the nondiagonal matrix elements are much smaller than the diagonal elements, the secular determinant may be expanded to give, as a first approximation, an energy lowering arising from the various excited configurations considered of[20]

$$^{1(3)}\Delta E=-\sum_{n=0}{}'[\{^{1(3)}H_{0n}-{}^{1(3)}S_{0n}{}^{1(3)}H_{00}\}^2/(^{1(3)}H_{00}-{}^{1(3)}H_{nn})], \quad (9)$$

where $^{1(3)}H_{00}$ is just the singlet (triplet) Heitler–London energy, and $^{1(3)}S_{0n}$ is the total overlap between the singlet (triplet) Heitler–London wavefunction and the nth excited configuration.

There are two classes of excited configurations to consider, the locally excited and the charge transfer.[4] It is the former class which we consider first.

A. Locally Excited Configurations

An arbitrary locally excited configuration has the form

$$^{1(3)}\Psi_{jk}=[2(1\pm S_{jk}^2)]^{-1/2}\{|\,\phi_j\bar{\chi}_k\,|\pm|\,\chi_k\bar{\phi}_j\,|\}, \quad (10)$$

where $\phi_j(\chi_k)$ is an unspecified orbital from the Löwdin–Shull set centered on Hydrogen Atom A (B). This arbitrary configuration is a two-electron excitation; the one-electron excitation is seen to be a special case of (10) with either ϕ_j or χ_k replaced by the corresponding $1s$ function. The energy of configuration (10) has the simple form

$$^{1(3)}H_{jk}=(1\pm S_{jk}^2)^{-1}\{\mathcal{J}_{jk}\pm\mathcal{K}_{jk}\}, \quad (11)$$

where $\mathcal{J}_{jk}$ and $\mathcal{K}_{jk}$ are defined by Eq. (4).

The nondiagonal matrix element between (10) and the starting function (1) of appropriate multiplicity is

$$^{1(3)}H_{00,jk}=[(1\pm S_{00}^2)(1\pm S_{jk}^2)]^{-1/2}\{\mathcal{J}_{00,jk}\pm\mathcal{K}_{00,jk}\}, \quad (12)$$

[19] Except for the lowest energy orbital which is identical with the original hydrogen $1s$ orbital.
[20] Equation (14) of Ref. 6.

$\mathcal{J}_{00,jk}$ and $\mathcal{K}_{00,jk}$ being defined as

$$\mathcal{J}_{00,jk}=\int 1s_a^*(1)\,1s_b^*(2)\,H\phi_j(1)\chi_k(2)\,d\tau_1 d\tau_2,$$

$$\mathcal{K}_{00,jk}=\int 1s_a^*(1)\,1s_b^*(2)\,H\phi_k(1)\chi_j(2)\,d\tau_1 d\tau_2. \quad (13)$$

The total overlap between (1) and (10) becomes

$$^{1(3)}S_{00,jk}=\pm[(1\pm S_{00}^2)(1\pm S_{jk}^2)]^{-1/2}S_{0j}S_{0k}. \quad (14)$$

Substituting (11), (12), and (14) into Eq. (9) yields after a bit of straightforward algebra the following expression for the resulting energy lowering:

$$^{1(3)}\Delta E=(1/^{1(3)}D)\{\mathcal{J}_{00,jk}^2\pm 2\mathcal{J}_{00,jk}\mathcal{K}_{00,jk}+\mathcal{K}_{00,jk}^2$$
$$\pm[2S_{0j}S_{0k}/(1\pm S_{00}^2)][\mathcal{J}_{00,jk}\pm\mathcal{K}_{00,jk}][\mathcal{J}_{00}\pm\mathcal{K}_{00}]$$
$$+[S_{0j}S_{0k}/(1\pm S_{00}^2)]^2[\mathcal{J}_{00}\pm\mathcal{K}_{00}]^2\}, \quad (15)$$

where

$$^{1(3)}D=(1\pm S_{jk}^2)\mathcal{J}_{00}-(1\pm S_{00}^2)\mathcal{J}_{jk}\pm(1\pm S_{jk}^2)\mathcal{K}_{00}$$
$$\mp(1\pm S_{00}^2)\mathcal{K}_{jk}. \quad (16)$$

We see that the energy lowerings fall into two classes: certain terms in Expression (15) which contribute equally to the energy lowering of both the Heitler–London singlet and triplet, and other terms which contribute unequally to the singlet and triplet states. We first look at the terms in (15) which are the same for both the singlet and triplet. Expanding $^{1(3)}D$ and keeping all terms to $\mathcal{O}(S^4)$,[21] we find the particularly simple expression

$$\Delta E=[\mathcal{J}_{00,jk}^2/(\mathcal{J}_{00}-\mathcal{J}_{jk})]+\mathcal{O}(S^4). \quad (17)$$

In the case of a two-electron local excitation we find that, due to the orthogonality of the Löwdin–Shull functions, the Coulomb integral, $\mathcal{J}_{00,jk}$ in (17), reduces to the purely two-electron electrostatic repulsion integral, namely,

$$J_{00,jk}=\int 1s_a^*(1)\,1s_b^*(2)\,r_{12}^{-1}\phi_j(1)\chi_k(2)\,d\tau_1 d\tau_2.$$

Expression (17) then resembles the well-known dispersion energy term which arises in the zero-overlap, no-exchange theory,[22] in which no distinction is made between the spin multiplicities of the combined system and in which all the $\mathcal{J}$'s reduce to J's. In analogy, then, we call those terms in (15) which contribute equally to both the singlet and triplet states the "*generalized dispersion energy.*" It is most interesting to see that the inclusion of both overlap and exchange does not affect this energy term, Eq. (17), except to $\mathcal{O}(S^4)$. Thus the neglect of overlap and exchange in calculating the dispersion energy of H_2, or any two interacting doublets for that matter, seems to be completely justified.

[21] For the Löwdin–Shull orbitals all overlap charge densities are of the form (algebraic factor) $\times\exp(-R)$. Hence $\mathcal{O}(S^4)$, even for excited orbitals, is extremely small.

[22] See Eq. (24) of Ref. 4.

We now look at the energy terms in (15) which contribute unequally to the singlet and triplet, thus serving to modify the original Heitler–London triplet–singlet separation. This factor, essentially a second-order exchange effect, we call a "generalized exchange-correlation" energy. It is convenient to examine this effect in terms of the *difference* in the generalized exchange-correlation lowerings, in other words in terms of the modification introduced in the Heitler–London triplet–singlet separation. We find for a virtual excitation of Type (10) that

$$\Delta(^3E-{}^1E)=[-\mathcal{J}_{00,jk}/(\mathcal{J}_{00}-\mathcal{J}_{jk})]\{4\mathcal{K}_{00,jk}-4S_{0j}S_{0k}\mathcal{J}_{00}$$
$$-[2\mathcal{J}_{00,jk}/(\mathcal{J}_{00}-\mathcal{J}_{jk})][S_{jk}^2\mathcal{J}_{00}-S_{00}^2\mathcal{J}_{jk}+\mathcal{K}_{00}-\mathcal{K}_{jk}]\}$$
$$+\mathcal{O}(S^4). \quad (18)$$

We remark that each of the terms here is of $\mathcal{O}(S^2)$ and that the expression lacks the simplicity of (17). Some of the terms arise from the nonorthogonality of the orbitals of sets $\{\phi_j\}$ and $\{\chi_k\}$ (inclusion of overlap); others are due to the introduction of electron exchange.

A simplification of (18) does occur in the case of a two-electron excitation when *both* excited orbitals are orthogonal to *both* hydrogen 1*s* orbitals, i.e.,

$$S_{1s_a}\chi_k=S_{1s_b}\phi_j=0. \quad (19)$$

In this case (18) reduces to

$$\Delta(^3E-{}^1E)=[J_{00,jk}/(\mathcal{J}_{00}-\mathcal{J}_{jk})]\{4K_{00,jk}$$
$$-[2J_{00,jk}/(\mathcal{J}_{00}-\mathcal{J}_{jk})][\mathcal{K}_{00}-\mathcal{K}_{jk}]\}. \quad (20)$$

Here the mixed Coulomb and exchange integrals, $\mathcal{J}_{00,jk}$ and $\mathcal{K}_{00,jk}$ in (18), reduce to purely two-electron repulsion ($J_{00,jk}$) and exchange ($K_{00,jk}$) integrals. Salem[5] has treated the general case of intersystem interaction at long range assuming all overlap integrals of Type (19) to be negligible. Salem's treatment, derived for the case of two interacting closed-shell systems, can be easily adapted to our case of two interacting doublets. Assuming equal singlet–singlet and triplet–triplet excitation energies, we find that Eq. (20) reduces to

$$\Delta(^3E-{}^1E)=-4J_{00,jk}K_{00,jk}/(\mathcal{J}_{00}-\mathcal{J}_{jk}), \quad (21)$$

where $\mathcal{J}_{00}-\mathcal{J}_{jk}$ is just the excitation energy in this zero-overlap approximation. The energy difference therefore appears purely as a "Coulomb-exchange" energy, corresponding to the difference between the triplet energy lowering of

$$-(J_{00,jk}-K_{00,jk})^2/\Delta W$$

and the analogous singlet lowering of

$$-(J_{00,jk}+K_{00,jk})^2/\Delta W.$$

Expression (21), containing the product of two inherently positive electrostatic two-electron integrals, is itself positive, thus serving to *increase* the triplet–singlet separation and improve the erroneous Heitler–London behavior. This zero-overlap picture thus ap-

pears qualitatively excellent. Two-electron locally excited configurations are seen to be responsible not only for a general lowering of both spin states, but also for a further energy separation between them, needed for a rectification of the Heitler–London wavefunction. We see in the next section, however, that this picture is essentially incorrect. Use of the correct expression (18) leads to conclusions entirely different from those resulting from the approximate expression (21).

B. Charge-Transfer Configurations

Charge-transfer configurations of both the one- and two-electron excitation type can be represented by the general wavefunction

$$^{1(3)}\Psi_{jk}=(1/\sqrt{2})\{|\,\phi_j\bar{\phi}_k\,|\pm|\,\phi_k\bar{\phi}_j\,|\}, \qquad (22)$$

where ϕ_j and ϕ_k are any orbitals chosen out of the set $\{\phi_i\}$ centered on Hydrogen Atom A, including the $1s$. There will be, of course, a configuration degenerate with (22) where the occupied orbitals are chosen from $\{\chi_i\}$. A configuration of Type (22) will have, in analogy with Expression (11), an energy of

$$^{1(3)}H_{jk}=\mathcal{J}_{jk}\pm\mathcal{K}_{jk}, \qquad (23)$$

where both the Coulomb and exchange integrals contain only one-center charge distributions.

The interaction between (22) and the "zero-order" wavefunction of appropriate multiplicity (1) has the form

$$^{1(3)}H_{00,jk}=(1\pm S_{00}^2)^{-1/2}\{\mathcal{L}_{00,jk}\pm\mathcal{L}_{00,kj}\}. \qquad (24)$$

Here the two "hybrid" integrals contain the product of a one-center charge distribution and an overlap charge distribution and are defined as

$$\mathcal{L}_{00,jk}=\int 1s_a^*(1)\,1s_b^*(2)\,H\phi_j(1)\,\phi_k(2)\,d\tau_1 d\tau_2,$$

$$\mathcal{L}_{00,kj}=\int 1s_a^*(1)\,1s_b^*(2)\,H\phi_k(1)\,\phi_j(2)\,d\tau_1 d\tau_2. \qquad (25)$$

Both of these integrals are seen to be of $\mathcal{O}(S^2)$.

Introducing the required energy and overlap terms into (9) will yield, as in the preceding section, formal expressions for the lowerings of the triplet and singlet Heitler–London functions. We consider these explicitly only for two cases of particular interest.

Looking first at the one-electron charge-transfer configuration where $\phi_j=1s$ in (22), we find that the total overlap between (22) and (1), the starting Heitler–London wavefunction of appropriate multiplicity, is

$$^{1(3)}S_{00,0k}=(1\pm S_{00}^2)^{-1/2}S_{0k}. \qquad (26)$$

In this case we obtain for the generalized dispersion lowering

$$E_{\text{gen disp}}=[1/(\mathcal{J}_{00}-\mathcal{J}_{0k})]\{\mathcal{L}_{00,0k}^2+\mathcal{L}_{00,k0}^2 -2S_{0k}\mathcal{L}_{00,0k}\mathcal{J}_{00}+S_{0k}^2\mathcal{J}_{00}^2\}+\mathcal{O}(S^3). \qquad (27)$$

The reader should notice that all the terms in the numerator are of $\mathcal{O}(S^2)$, in contrast with the expression for the generalized dispersion energy in the case of a double local excitation (17) which is of zeroth order in overlap. Likewise, we find for the one-electron charge-transfer configuration under consideration a generalized exchange-correlation contribution of the form

$$\Delta(^3E-^1E)=[-4/(\mathcal{J}_{00}-\mathcal{J}_{0k})]\{\mathcal{L}_{00,0k}\mathcal{L}_{00,k0}+S_{0k}\mathcal{L}_{00,k0}\mathcal{J}_{00}\} +\mathcal{O}(S^4), \qquad (28)$$

which is also of $\mathcal{O}(S^2)$.

Another charge-transfer configuration is of interest. This is the case of a two-electron excitation to the *same* excited orbital ϕ_k, a configuration only possible as a singlet. In this case (22) reduces to

$$^1\Psi_{kk}=|\,\phi_k\bar{\phi}_k\,|. \qquad (29)$$

Since this type of configuration does not exist as a triplet, all of the energy lowering must be of the generalized exchange-correlation type, serving to modify the original Heitler–London triplet–singlet separation. Since Configuration (29) is orthogonal to (1), we find a particularly simple expression for this generalized exchange-correlation contribution

$$\Delta(^3E-^1E)=[-2\mathcal{L}_{00,kk}^2/(\mathcal{J}_{00}-\mathcal{J}_{kk})]+\mathcal{O}(S^4). \qquad (30)$$

This expression has a certain similarity with (17); however, here, as in (27) and (28), the leading term is of $\mathcal{O}(S^2)$. We see in the next section that excited states of the type (29) play an important role in the correction of the erroneous Heitler–London triplet–singlet separation.

One should notice that the generalized exchange-correlation contribution of the two-electron locally excited states of the form (10) and *all* the energy contributions of the charge-transfer states are of $\mathcal{O}(S^2)$. As Murrell *et al.* have pointed out,[4] it is thus impossible to separate rigorously the contributions arising from charge-transfer states from certain of the energy lowerings introduced by locally excited states.

IV. MULTICONFIGURATION CALCULATION

To illustrate the formal results of the preceding section and to investigate the importance of various excited configurations for both the individual lowering of the Heitler–London singlet and triplet as well as for the improvement of the initial triplet–singlet separation we have performed a many-configuration calculation for the hydrogen molecule at an internuclear separation of 8 a.u. This distance was chosen as being large enough to illustrate the poor asymptotic behavior of the Heitler–London wavefunction yet not so large that the interaction energies become physically negligible.

At this distance we find for the Heitler–London singlet and triplet energies [Eq. (3)]

$$^1E_0=-1.00001739 \text{ a.u.}, \quad ^3E_0=-0.99998618 \text{ a.u.}, \qquad (31)$$

to be compared with the accurate results of Kołos and Wolniewicz,[13] namely,

$$^1E=-1.0000528 \text{ a.u.}, \qquad ^3E=-1.0000196 \text{ a.u.} \quad (32)$$

Nine excited configurations were used in the actual calculation. The results are collected in Table II. Listed are the lowerings of the initial singlet and triplet states as calculated from (9), the generalized exchange-correlation contribution of the particular configurations to a modification of the Heitler–London triplet–singlet separation, and the generalized dispersion lowering as defined in the previous section. The results of this calculation as well as the Heitler–London and Kołos and Wolniewicz state energies are shown schematically in Fig. 3. It is most useful to discuss these numerical results in terms of the particular type of excited configuration.

A. One-Electron Local Excitation

Only one configuration of this type was considered, that formed by exciting one electron from a $1s$ orbital to the $2p_\sigma$ orbital centered on the same atom, giving

$$^{1(3)}\Psi=N\{|\,1s_a2\bar{p}_{\sigma_b}\,|\pm|\,2p_{\sigma_b}1\bar{s}_a\,|+|\,2p_{\sigma_a}1\bar{s}_b\,|\pm|\,1s_b2\bar{p}_{\sigma_a}\,|\}, \quad (33)$$

N being a normalization factor. The generalized dispersion lowering introduced by (33) is virtually negligible. This is not surprising, since in the zero-overlap, no-exchange theory this type of configuration gives rise to the so-called "induction" or "polarization" energy[2,3] which, even for systems with a permanent dipole moment, is unimportant energetically.[23] Furthermore the generalized exchange-correlation contribution of (33) is of negligible size. Since this configuration gave a totally unimportant contribution to the interaction energy, no other configurations of this type were considered.

TABLE II. Configuration interaction for H_2 ($R=8$ a.u.) (energy lowerings in a.u.$\times10^{-6}$).

Excited configuration[a]	$^1\Delta E$	$^3\Delta E$	$\Delta E_{\text{gen exch}}$ $(^3\Delta E-{}^1\Delta E)$	$E_{\text{gen disp}}$
$1s_a2p_{\sigma_b}$	−0.003	−0.001	0.002	−0.002
$2p_{\sigma_a}2p_{\sigma_b}$	−15.152	−14.859	0.293	−15.01
$2p_{\pi_a}2p_{\pi_b}$	−7.682	−7.533	0.149	−7.608
$2s_a2s_b$	−0.000	−0.000	0.000	−0.000
$2s_a2p_{\sigma_b}$	−0.001	−0.001	0.000	−0.001
$1s_a1s_a$	−0.628	···	0.628	···
$1s_a2p_{\sigma_a}$	−0.085	−0.401	−0.316	−0.243
$2p_{\sigma_a}2p_{\sigma_a}$	−2.255	···	2.255	···
$2p_{\pi_a}2p_{\pi_a}$	−0.180	···	0.180	···
Total	−25.986	−22.795	3.191[b]	−22.863
$2p_{\sigma_a}2p_{\sigma_b}$[c]	−5.836	−5.052	0.784	−5.444
$2p_{\sigma_a}2p_{\sigma_a}$[c]	−2.116	···	2.116	···

[a] Numerical values take into account all possible degeneracies for each listed configuration.

[b] Exact value 2.12×10^{-6} a.u.

[c] $\zeta_{2p}=\frac{1}{2}$; see Sec. IV of this paper.

[23] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 988.

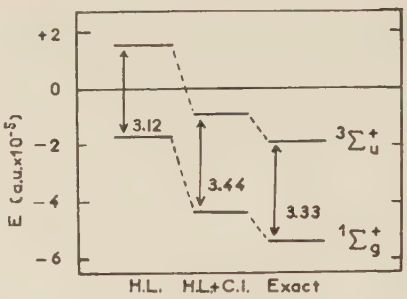

FIG. 3. Improvement of the Heitler–London lowest singlet and lowest triplet energies for H_2 at $R=8$ a.u. brought about by configuration interaction. The exact level spacings are taken from Kołos and Wolniewicz (Ref. 13 of this paper).

B. Two-Electron Local Excitation

Four configurations of this type were considered. The first two were those known to give the correct orientation of transition dipoles important for the dispersion energy in the zero-overlap, no-exchange treatment of interatomic forces,

$$^{1(3)}\Psi=N\{|\,2p_{\sigma_a}2\bar{p}_{\sigma_b}\,|\pm|\,2p_{\sigma_b}2\bar{p}_{\sigma_a}\,|\},$$
$$^{1(3)}\Psi=N\{|\,2p_{\pi_a}2\bar{p}_{\pi_b}\,|\pm|\,2p_{\pi_b}2\bar{p}_{\pi_a}\,|\}.^{24} \quad (34)$$

As we expect from the previous section, these same states give an important generalized dispersion lowering. At a distance of 8 a.u. they are responsible for 67% of what may be called the total generalized dispersion energy,

$$E_{\text{gen disp}}\approx{}^3E_0-{}^3E. \quad (35)$$

(We see in Sec. IV.D that the generalized exchange-correlation energy affects mainly the energy of the singlet state.) The reader might note that these two configurations alone account for 91% of the dipole–dipole contribution to the dispersion energy in the zero-overlap, no-exchange approximation.[25]

The two configurations (34) lead to a small generalized exchange-correlation contribution, lowering slightly the singlet with respect to the triplet.[26] If, however, we had calculated this contribution using the approximate expression (21), we would have obtained, specifically from the configuration $2p_{\sigma_a}2p_{\sigma_b}$, a *far too large* result, yielding a triplet–singlet separation much greater than its true value. The terms in (18) containing overlap explicitly [all of $\mathcal{O}(S^2)$] are no less important numerically than those which involve overlap only implicitly and which are kept in (21) [also of $\mathcal{O}(S^2)$].

[24] There are, of course, two degenerate states possible from this π-type configuration.

[25] R. J. Bell, Proc. Phys. Soc. (London) **86**, 549 (1965).

[26] The discrepancy between our results and those of Hirschfelder and Linnett (Ref. 14) arises from the fact that they obtain a large generalized exchange-correlation contribution from Configuration (34) favoring the *triplet* state.

Musher and Salem[6] have pointed out that the *total* intersystem interaction energy can be well approximated by neglecting intersystem overlap. For a study of the triplet–singlet separation, itself of $\mathcal{O}(S^2)$, a neglect of overlap is no longer valid.

The remaining two-electron locally excited configurations considered were

$$^{1(3)}\Psi = N\{|\, 2s_a 2\bar{s}_b \,| \pm |\, 2s_a 2\bar{s}_b \,|\},$$

$$^{1(3)}\Psi = N\{|\, 2s_a 2\bar{p}_{\sigma_b} \,| \pm |\, 2p_{\sigma_b} 2\bar{s}_a \,| \pm |\, 2s_b 2\bar{p}_{\sigma_a} \,| + |\, 2p_{\sigma_a} 2\bar{s}_b \,|\}. \quad (36)$$

Since neither of these configurations leads to an important transition multipole interaction, we expect the consequent generalized dispersion contribution to be small. This is indeed the case (Table III); these configurations give a totally negligible contribution to the generalized dispersion energy as well as to the generalized exchange-correlation energy.

C. One-Electron Charge Transfer

Two configurations of this form were considered. It would be natural to introduce the so-called "polar" or "ionic" configuration

$$^1\Psi = N\{|\, 1s_a 1\bar{s}_a \,| + |\, 1s_b 1\bar{s}_b \,|\}. \quad (37)$$

This configuration is known to give an important energy contribution in the molecular region properly speaking, where it is introduced to correct for the Heitler–London *overcorrelation* mentioned above.[16] This configuration being possible only as a singlet, all the energy lowering arising from (37) will be of the generalized exchange-correlation type. The function (37) yields a moderate increase in the triplet–singlet separation.

The second one-electron charge-transfer configuration considered was the following:

$$^{1(3)}\Psi = N\{|\, 1s_a 2\bar{p}_{\sigma_a} \,| \pm |\, 2p_{\sigma_a} 1\bar{s}_a \,| \pm |\, 1s_b 2\bar{p}_{\sigma_b} \,| + |\, 2p_{\sigma_b} 1\bar{s}_b \,|\}. \quad (38)$$

We find that this configuration contributes mainly to the generalized exchange-correlation energy, leading to a slight decrease in the Heitler–London triplet–singlet separation.

D. Two-Electron Charge Transfer

Two configurations of this sort were considered, both of the type (29), namely, a two-electron virtual excitation to the *same* excited orbital. Both configurations are thus possible only as a singlet, and hence their entire energy contribution is of the generalized exchange-correlation type. The first configuration considered was

$$^1\Psi = N\{|\, 2p_{\pi_a} 2\bar{p}_{\pi_a} \,| + |\, 2p_{\pi_b} 2\bar{p}_{\pi_b} \,|\}, \quad (39)$$

which is, of course, to be taken as two degenerate π configurations. We find that (39) contributes only extremely slightly to a modification of the original triplet–singlet separation.

The second two-electron charge-transfer configuration considered was

$$^1\Psi = N\{|\, 2p_{\sigma_a} 2\bar{p}_{\sigma_a} \,| + |\, 2p_{\sigma_b} 2\bar{p}_{\sigma_b} \,|\}. \quad (40)$$

We find that this one configuration alone leads to an important modification in the initial triplet–singlet splitting, increasing this separation and hence correcting the faulty Heitler–London behavior. Configuration (40) yields a generalized exchange-correlation contribution equal in magnitude to the difference between the Heitler–London and exact (Herring and Flicker[8,11]) triplet–singlet separations. An interpretation of the importance of this configuration in terms of electron correlation is given in the final section.

Charge-transfer states have been proposed as being important in molecular or atomic interactions when the two interacting species differ in electronegativity.[4] It is interesting to notice their importance here in a case of identical electronegativities, where the charge-transfer configurations are introduced not to correct for an appreciable ionic character of the ground state of the combined system, but rather to account for an additional correlation between the two electrons.

V. DISCUSSION

We have seen that an actual multiconfiguration calculation for the hydrogen molecule at an internuclear distance of 8 a.u. yielded an important correction to the initial Heitler–London triplet–singlet separation. In

TABLE III. Correlation effects in H_2 ($R=8$ a.u.).

$r_{a_2}\cos\theta_{a_2}$	$r_{a_1}=1$, $r_{b_1}=7$		$r_{a_1}=3$, $r_{b_1}=5$	
	$\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)$ L.E.[a]	$\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)$ C.T.[b]	$\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)$ L.E.[a]	$\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)$ C.T.[b]
−2	$4e^{-16}$	$2e^{-10}$	$10e^{-14}$	$6e^{-12}$
−1	$5e^{-16}$	$2e^{-10}$	$5e^{-12}$	$3e^{-10}$
0	$-8e^{-16}$	$-8e^{-22}$	$-24e^{-16}$	$-40e^{-16}$
1	$-28e^{-16}$	$-2e^{-10}$	$-5e^{-12}$	$-3e^{-10}$
2	$-6e^{-14}$	$-2e^{-10}$	$-10e^{-14}$	$-6e^{-12}$
3	$-5e^{-12}$	$-3e^{-10}$	$-54e^{-16}$	$-18e^{-14}$
4	$-4e^{-10}$	$-4e^{-10}$	$-12e^{-14}$	$-12e^{-14}$
5	$-3e^{-8}$	$-5e^{-10}$	$-9e^{-12}$	$-25e^{-14}$
6	$-2e^{-6}$	$-6e^{-10}$	$-6e^{-10}$	$-10e^{-12}$
7	$-e^{-4}$	$-8e^{-10}$	$-3e^{-8}$	$-5e^{-10}$
8	$-56e^{-16}$	$-8e^{-10}$	$-40e^{-16}$	$-24e^{-14}$
9	e^{-4}	$-8e^{-10}$	$3e^{-8}$	$5e^{-10}$
10	$2e^{-6}$	$-9e^{-10}$	$6e^{-10}$	$10e^{-12}$

[a] Two-electron local excitation (34).
[b] Two-electron charge transfer (40).

fact the modified value for this splitting is now slightly too large. We expect two factors to compensate for this. Other excited configurations of the type (38) should contribute to a slight decrease in the triplet–singlet separation. Furthermore, in the calculation described above we consider separately the interaction between each excited configuration and the ground configuration of appropriate multiplicity [Eq. (9)], neglecting the interactions between the various excited configurations. In an exact solution of the secular determinant these would have to be taken into account. For our calculation the only large "third-order" interaction is between the charge-transfer configuration (40) and the two-electron locally excited configuration $2p_{\sigma_a}2p_{\sigma_b}$. Including this third-order term reduces the value of the modification in the triplet–singlet separation from 3.19×10^{-6} to 2.35×10^{-6} a.u.

The calculation also yields ~68% of the total generalized dispersion energy, almost all of which arises from the two-electron locally excited configurations. We expect the remaining generalized dispersion energy to be contained in the higher transition multipole interactions which we have not considered, namely the dipole–quadrupole, dipole–octopole, and quadrupole–quadrupole terms. These could be introduced by certain two-electron locally excited configurations containing the various $3d$ orbitals. In line with the results of the preceding section we do not expect these locally excited configurations to give an important generalized exchange-correlation contribution. In other words the remaining generalized dispersion energy could be obtained from configurations which would not significantly effect the triplet–singlet separation.

We see that the partition of the energy into a generalized dispersion energy and a generalized exchange-correlation energy initially proposed in Sec. III is physically useful. Certain states, namely the two-electron local excitations, are responsible for the major part of the generalized dispersion energy, contributions which are essentially unchanged from those predicted by the zero-overlap, no-exchange theory. Other states, specifically the charge-transfer configurations, are responsible for a generalized exchange-correlation contribution, giving rise to the expected correction to the initial Heitler–London triplet–singlet separation.

Herring[8] has warned against using a limited configuration-interaction treatment with isolated hydrogen-atom orbitals to obtain the true behavior of the triplet–singlet splitting. This is because the excited hydrogen orbitals with a radial dependence of $r^n\times\exp(-r/n)$ give rise to overlap charge densities going to zero slower than $\exp(-R)$, which is the proper decay factor for the H_2 system.[7] Herring predicted that the singlet–triplet separation obtained from a configuration-interaction treatment using the isolated hydrogen orbitals would behave as an alternating series with a slow convergence. To see the effect of this we have tried mixing the Heitler–London wavefunction with the two-electron locally excited configuration

$$^{1(3)}\Psi=N\{|\,2p_{\sigma_a}2\bar{p}_{\sigma_b}\,|\pm|\,2p_{\sigma_b}2\bar{p}_{\sigma_a}\,|\},\qquad(34)$$

as well as with the two-electron charge-transfer configuration

$$^{1}\Psi=N\{|\,2p_{\sigma_a}2\bar{p}_{\sigma_a}\,|+|\,2p_{\sigma_b}2\bar{p}_{\sigma_b}\,|\},\qquad(40)$$

where the $2p_\sigma$ orbitals are the true hydrogen-atom orbitals, namely

$$2p_\sigma=(1/2^5\pi)^{1/2}r\cos\theta\exp(-\tfrac{1}{2}r).\qquad(41)$$

The result of mixing in these two excited configurations is shown in the last line of Table II. Using the Löwdin–Shull $2p$ orbital, we found State (34) to be responsible for ~45% of the total generalized dispersion energy. With an orbital exponent of $\zeta_{2p}=\frac{1}{2}$, however, the generalized dispersion contribution of (34) drops markedly.[27] As for the generalized exchange-correlation contribution of (34) with $\zeta_{2p}=\frac{1}{2}$, it is about three times larger than that arising from the same configuration but with the Löwdin–Shull $2p$ orbital, but still relatively small.

Using the Löwdin–Shull set, we found Configuration (40) to give an important generalized exchange-correlation energy contribution to the rectification of the Heitler–London triplet–singlet separation. With a $2p$ hydrogenic orbital the result is essentially unchanged. There does not, consequently, seem to be evidence for an alternating-series type of convergence where the contributions of individual excited configurations to the triplet–singlet separation are much greater in magnitude than the discrepancy between the Heitler–London and exact values.[28]

The reader might notice that the manifold of one- and two-electron locally excited states as well as the corresponding ensemble of charge-transfer states is overcomplete. When overlap is taken into account at all stages of a configuration-interaction treatment the problem of overcompleteness does not lead to mathematical difficulties.[29] We should also realize[4] that the manifold of locally excited states alone would be sufficient to obtain a correct value of the triplet–singlet separation as well as the total generalized dispersion

[27] We find that the generalized dispersion lowering introduced by State (34) is, to four significant figures, exactly that predicted by the approximate formula (17) even though the exchange integral, $\mathcal{K}_{00,jk}$, is 40 times greater in magnitude than the Coulomb integral which appears in (17). We see here a confirmation of the formal result of Sec. III that the generalized dispersion energy is independent of overlap.

[28] For the generalized dispersion energy the convergence will be faster using the Löwdin–Shull orbitals in place of the true hydrogen orbitals. Indeed, with hydrogen-atom solutions as a basis set, it is necessary to use continuum wavefunctions to obtain all of the dispersion energy in the zero-overlap, no-exchange approximation; see R. Eisenschitz and F. London, Z. Physik **60**, 491 (1930).

[29] If an overcomplete set is used and assumed orthogonal, the secular determinant will vanish due to the inevitable linear dependencies; see P.-O. Löwdin, Advan. Chem. Phys. **2**, 277 (1959).

energy for the H_2 system. In principle each charge-transfer state could be expanded as a linear combination of suitable locally excited states. At large distances, however, the convergence of such an expansion would be quite slow. Our use of charge-transfer states is strictly pragmatic, the choice being made for computational ease.

VI. PHYSICAL INTERPRETATION

Herring[8] attributes the poor behavior of the Heitler–London triplet–singlet separation to a lack of adequate correlation between the two electrons in the exchange region. In this section we examine the correlation introduced by a configuration largely responsible for the dispersion energy, $2p_{\sigma_a}2p_{\sigma_b}$, and by a configuration giving rise to an important modification in the triplet–singlet splitting, namely the charge-transfer configuration (40). This latter configuration lowers only the singlet; and the lowering of the generalized dispersion type introduced by $2p_{\sigma_a}2p_{\sigma_a}$ is identical for the singlet and triplet. We thus consider for comparison the correlation introduced by these two configurations into the Heitler–London singlet ground state.

For this state the two-electron probability distribution function (the spinless second-order density matrix[3]) is

$$^1\rho_0(2:\mathbf{r}_1,\mathbf{r}_2)\sim\{1s_a^2(1)1s_b^2(2)+1s_b^2(1)1s_a^2(2)+21s_a(1)1s_b(1)1s_a(2)1s_b(2)\}. \quad (42)$$

Using the coordinate system of Fig. 2, we find that (42) becomes

$$^1\rho_0(2:\mathbf{r}_1,\mathbf{r}_2)\sim\{\exp(-r_{a_1})\exp(-r_{b_2})+\exp(-r_{a_2})\exp(-r_{b_1})\}^2. \quad (43)$$

A configuration interaction between the Heitler–London singlet function (1) and the following two-electron locally excited configuration

$$^1\Psi=N\{|\,2p_{\sigma_a}2\bar{p}_{\sigma_b}\,|+|\,2p_{\sigma_b}2\bar{p}_{\sigma_a}\,|\} \quad (34)$$

leads, to first order, to the following modification in the two-electron distribution function:

$$^1\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)\sim-\{1s_a(1)2p_{\sigma_a}(1)1s_b(2)2p_{\sigma_b}(2)+1s_b(1)2p_{\sigma_b}(1)1s_a(2)2p_{\sigma_a}(2)+1s_a(1)2p_{\sigma_b}(1)\times1s_b(2)2p_{\sigma_a}(2)+1s_b(1)2p_{\sigma_a}(1)1s_a(2)2p_{\sigma_b}(2)\}, \quad (44)$$

which reduces to

$$^1\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)\sim-\{r_{a_1}\cos\theta_{a_1}r_{t_2}\cos\theta_{b_2}\exp(-2r_{a_1})\times\exp(-2r_{b_2})+r_{b_1}\cos\theta_{b_1}r_{a_2}\cos\theta_{a_2}\exp(-2r_{b_1})\times\exp(-2r_{a_2})+[r_{a_1}\cos\theta_{a_1}r_{b_2}\cos\theta_{b_2}+r_{b_1}\cos\theta_{b_1}r_{a_2}\times\cos\theta_{a_2}]\exp(-r_{a_1})\exp(-r_{b_1})\exp(-r_{a_2})\times\exp(-r_{b_2})\}. \quad (45)$$

The presence of a minus sign in (44) and (45) arises from the fact that, due to the sign of the nondiagonal matrix element, the coefficients in the final wavefunction of the initial Heitler–London wavefunction (1) and the excited configuration (34) will be of opposite sign.

Likewise the two-electron charge-transfer configuration (40) introduces a modification in the two-electron distribution function of

$$^1\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)\sim-\{1s_a(1)2p_{\sigma_a}(1)1s_b(2)2p_{\sigma_a}(2)+1s_b(1)2p_{\sigma_a}(1)1s_a(2)2p_{\sigma_a}(2)+1s_a(1)2p_{\sigma_b}(1)\times1s_b(2)2p_{\sigma_b}(2)+1s_b(1)2p_{\sigma_b}(1)1s_a(2)2p_{\sigma_b}(2)\}, \quad (46)$$

which, in turn, reduces to

$$^1\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)\sim-\{r_{a_1}\cos\theta_{a_1}r_{a_2}\cos\theta_{a_2}[\exp(-2r_{a_1})\times\exp(-r_{b_2})\exp(-r_{a_2})+\exp(-r_{a_1})\exp(-r_{b_1})\times\exp(-2r_{a_2})]+r_{b_1}\cos\theta_{b_1}r_{b_2}\cos\theta_{b_2}[\exp(-r_{a_1})\times\exp(-r_{b_1})\exp(-2r_{b_2})+\exp(-2r_{b_1})\exp(-r_{a_2})\times\exp(-r_{b_2})]\}. \quad (47)$$

The importance of an excited configuration for electron correlation can be measured by the magnitude of this first-order change in the two-electron distribution function. In like manner, the "kind" of correlation introduced is reflected in the particular value of $\mathbf{r}_1$ and $\mathbf{r}_2$ for which $^1\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)$ takes on a large, positive value. A large value of $^1\Delta\rho(2:\mathbf{r}_1,\mathbf{r}_2)$ indicates that the particular excited configuration introduces a strong additional correlation between the electrons when they are simultaneously at $\mathbf{r}_1$ and $\mathbf{r}_2$. A positive (negative) sign indicates an increased (decreased) probability of finding the electrons simultaneously at $\mathbf{r}_1$ and $\mathbf{r}_2$ compared with the initial two-electron probability (43).

We chose to examine the behavior of these two first-order changes in the two-electron distribution function in several simple cases. We first fix Electron 1 at 1 a.u. along the internuclear axis ($r_{a_1}=1$, $r_{b_1}=7$), then at 3 a.u. along the same axis ($r_{a_1}=3$, $r_{b_1}=5$). Electron 2 is then allowed to take on a series of positions along the internuclear axis. For each of these cases the leading term in the expressions (45) and (47) is given in Table III. Examination of these results is most interesting. We see that the two-electron local excitation (34) introduces correlation essentially when the two electrons are on *opposite sides* of a median plane perpendicular to the intermolecular axis, a correlation which is strongest when both electrons are close to their respective hydrogen atoms. Furthermore, when one electron is between Hydrogen Atoms A and B, there is an increased tendency of finding the other electron *outside* the interatomic region. This is none

other than the "Coulomb" correlation known to be the cause of the London dispersion forces.[30,31]

Relative to this Coulomb correlation, the correlation introduced by the two-electron charge-transfer configuration (40) is strongest when the electrons are on the *same side* of above-mentioned median plane. This correlation effect is essentially unchanged whether the electrons are near (1 a.u.) or far (3 a.u.) from one of the hydrogen atoms. The charge-transfer configuration introduces a "*same-side*" correlation between the electrons, which is hardly present in the Coulomb correlation effect arising from the locally excited configuration. Here too, as in the case of Coulomb correlation, if one electron is *inside* the interatomic region, there is an increased probability of finding the other outside.

The defect of the Heitler–London description at large distances thus seems to be that the singlet wavefunction allows the electrons to approach each other too closely in the region of one of the hydrogen atoms. In the triplet state, of course, this is prohibited by the exclusion principle. By introducing a long-range correlation between the electrons (Coulomb correlation), two-electron locally excited configurations lower equally the singlet and triplet without correcting for the above singlet deficiency. Certain charge-transfer configurations introduce the required short-range (same side) correlation.

Note added in proof: After careful consideration, the authors feel that the simpler term "*generalized exchange*" energy could possibly replace the name "generalized exchange-correlation" energy.

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TABLE IV. Hybrid integrals.

$L_{\alpha\beta\gamma\bar{\delta}} = \int \alpha_a^*(1)\beta_a^*(2) r_{12}^{-1} \gamma_a(1)\delta_b(2) d\tau_1 d\tau_2$

$L_{1s1s1s1\bar{s}} = 2.7387379\times10^{-3}$	
$L_{1s1s2\sigma1\bar{s}} = 4.4672576\times10^{-4}$	
$L_{1s2\sigma1s1\bar{s}} = 7.9558529\times10^{-3}$	
$L_{1s2\sigma2\sigma1\bar{s}} = 1.4792190\times10^{-3}$	
$L_{1s2\pi2\pi1\bar{s}} = 1.6942500\times10^{-4}$	
$L_{1s2\sigma2\sigma1\bar{s}} = 2.9184\times10^{-3}$ $(\zeta_{2p}=\frac{1}{2})$	

TABLE V. Exchange integrals.

$C_{\alpha\beta\gamma\delta} = \int \alpha_b^*(1)\beta_a^*(2) r_{12}^{-1} \gamma_a(1)\delta_b(2) d\tau_1 d\tau_2$

$C_{1s1s1s1s} = 3.2895902\times10^{-5}$	$C_{1s2\sigma2\sigma1s} = 5.7407369\times10^{-4}$
$C_{1s1s1s2\sigma} = 1.3158360\times10^{-4}$	$C_{1s1s2\pi2\pi} = 9.8683776\times10^{-6}$
$C_{1s2s1s2s} = 1.9140641\times10^{-4}$	$C_{2s2s2s2s} = 1.1273241\times10^{-3}$
$C_{1s1s2s2s} = 2.1466587\times10^{-4}$	$C_{2\sigma2\sigma2\sigma2\sigma} = 4.3179229\times10^{-3}$
$C_{1s1s2s2\sigma} = 3.2118950\times10^{-4}$	$C_{2\sigma2\sigma2\pi2\pi} = 1.7881670\times10^{-4}$
$C_{1s2\sigma1s2\sigma} = 3.7031675\times10^{-4}$	$C_{2\pi2\pi2\pi2\pi} = 1.2792812\times10^{-4}$
$C_{1s1s2\sigma2\sigma} = 4.7859516\times10^{-4}$	$C_{2\pi2\pi2\pi'2\pi'} = 6.6370549\times10^{-5}$
$C_{1s1s2\sigma2\sigma} = 6.40459\times10^{-3}$ $(\zeta_{2p}=\frac{1}{2})$	
$C_{2\sigma2\sigma2\sigma2\sigma} = 3.92526\times10^{-2}$ $(\zeta_{2p}=\frac{1}{2})$	

APPENDIX

The various energy integrals required in our calculation were evaluated following the treatments of Roothaan[32] and Kotani *et al.*[33] The numerical values were checked with the available results of Hirschfelder and Linnett[14] and Kotani *et al.*[33] In the case of the two-center, two-electron hybrid and exchange integrals the required G and W auxiliary functions were taken whenever possible from the very complete table compiled by Miller, Gerhauser, and Matsen.[34] Since these integrals are often tedious to work out, we give in Tables IV and V the values of integrals of these types which occurred in our calculation. The internuclear distance is 8 a.u. and, unless otherwise stated, the value of the orbital exponent for all orbitals is taken equal to unity. The orbitals are chosen as in Kotani *et al.*[33] except that the $2p_\sigma$ orbitals are taken to be both pointing toward the molecular center. The integral values are accurate to the number of significant figures given.

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